

Techno-Economic Feasibility of Extracting Minerals from Desalination Brines

I.S. AL-MUTAZ and K.M. WAGIALLA

Department of Chemical Engineering, King Saud University, P.O. Box 800, Riyadh 11421 (Saudi Arabia), Tel. 4676870

(Received January 22, 1988; in revised form April 24, 1988)

SUMMARY

Extraction of minerals from desalination brines represents a potentially important source of minerals. It is usually recommended for reducing fresh water production cost and minimizing waste disposal. In this paper, a techno-economic appraisal for the production of sodium chloride and caustic soda from Saudi desalination brines is presented.

Keywords: minerals, desalination, seawater, brine, sodium chloride, caustic soda.

INTRODUCTION

The Arabian Gulf countries have about 60% of the total world desalting capacity at the end of 1984. Table I shows the world desalting market in 1985. About 67.6% of the total capacity installed are of the multi-stage flash (MSF) type. Moreover, the MSF plants account for over 84% of the large size plants erected so far.

In the Arabian peninsula, the installed desalination capacity increased from 0.5×10^6 m³/d in 1973 to 5.8×10^6 m³/d in 1984, over a ten-fold increase. The capacity of the large plants installed during this period were as follows:

Jubail II plant, Saudi Arabia	253.5 mgd
Um El-Nar plant, Abu Dhabi	95.0 mgd
Jeddah IV, Saudi Arabia	58.0 mgd
Al-Khobar II, Saudi Arabia	51.0 mgd
Doha plant, Qatar	50.0 mgd
Shuaiba, Kuwait	45.0 mgd

Table II shows the desalination inventory of the Arabian Gulf countries.

Due to these large capacities, mineral extraction from the desalination blow-down is a major point of consideration in Arabian Gulf countries at the present

TABLE I

World desalting market, 1985 [3]

Total number of plants	4600
Total capacity	2621 mgd ($9.92 \times 10^6 \text{ m}^3/\text{d}$)
% MSF capacity	67.6
% RO capacity	23.0
<i>Geographical distribution</i>	
Arabian peninsula	60.0%
U.S.A.	17.0%
Libya	5.4%
Iran	3.1%
USSR	2.5%
Plant size <0.01 mgd: MSF	44.0%
RO	43.0%
> 1.00 mgd: MSF	84.5%
RO	11.2%

TABLE II

Desalination inventory of the Arab Gulf countries, 1984

Country	No. of units	Capacity		% of the world	Plant type (% share)				
		(mgd)	($\times 10^6 \text{ m}^3/\text{d}$)		MSF	VC	RO	EP	MED
Saudi Arabia	874	787.4	2.98	30.0	80.7	0.5	16.2	2.60	-
United Arab Emirates	279	288.0	1.09	11.0	95.5	1.6	1.8	0.55	0.25
Kuwait	99	269.5	1.02	10.2	98.3	-	0.9	0.50	-
Qatar	47	81.9	0.31	3.1	97.9	0.7	-	-	0.90
Bahrain	143	68.7	0.26	2.6	56.7	0.8	37.2	4.9	0.40
Oman	41	26.4	0.10	1.0	91.1	1.7	1.9	0.9	-
Total	1483	1521.9	5.76	57.9	86.7	0.65	10.7	1.8	0.15

time. This is due to the huge amounts of treated blowdown that is daily discharged back to the sea. Seawater concentration in the Arabian Gulf countries is considered among the highest concentrations in the world, 41,000–45,000 ppm.

Seawater constituents can be divided into the following categories:

— Major elements with concentrations of more than 100 ppm, such as chlorine, sodium, magnesium, sulfur, calcium and potassium.

TABLE III

Major constituents of seawater, ppm

Constituent	Normal seawater	Arabian Gulf	Red Sea
Chloride, Cl^-	18,980	23,000	22,219
Sodium, Na^+	10,550	15,850	14,255
Sulfate, SO_4^{2-}	2,649	3,200	3,078
Magnesium, Mg^{2+}	1,272	1,765	742
Calcium, Ca^{2+}	400	500	225
Potassium, K^+	380	460	210
Bicarbonate, HCO_3^-	140	142	146
Strontium, Sr^{2-}	13	-	-
Bromide, Br^-	65	80	72
Fluoride, F^-	1	-	-
Silicon, Si^{4-}	1	1.5	-
Iodide, I^-	-	-	-
Total dissolved salt	34,483	45,000	41,000

— Minor elements which have concentrations between 1 and 100 ppm. These include bromine, carbon, boron and fluorine.

— Traces of all other elements with concentrations below 1 ppm. These elements have a total concentration well below 0.24%.

The major constituents of the Red Sea and the Arabian Gulf water are presented in Table III and compared to those of normal seawater. Five compounds, or six elements, represent about 98% of the total mineral concentration. These are sodium sulfate, magnesium chloride and potassium chloride. Sodium chloride and magnesium chloride are in considerable demand in the world market because they can be used to produce various high-value products.

In this study, the techno-economic aspects related to the production of sodium chloride and its electrolysis to produce hydrogen and caustic soda will be investigated.

The purpose of mineral recovery from MSF desalination plants in the Arabian Gulf countries will be the reduction of the fresh water production cost and the minimization of marine pollution problems. This is accomplished by producing saleable products from the desalination effluents. MSF plants only are considered because they usually have large capacities and are normally associated with the production of surplus electric power.

PROCESS DESCRIPTION

General considerations

As shown in Fig. 1, the overall plant consists of two main units: the crystallization unit and the electrolytic cells for production of NaOH , Cl_2 and H_2 .

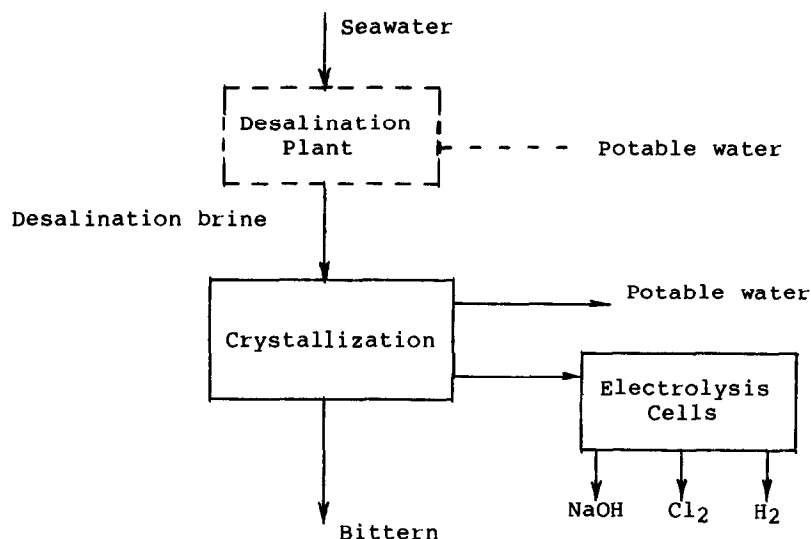


Fig. 1. Plant flow diagram for the production of NaOH, Cl₂ and H₂ from desalination brine.

Seawater has a concentration of about 35,000 ppm. For salts to precipitate in appreciable quantities for removal, seawater must be concentrated about eight times. This means that about 87.5% of its mass must be removed as water vapour.

Since the project under consideration is connected as a downstream plant with a desalination plant, the feedstock to a mineral extraction plant would be the highly concentrated brines (with a TDS concentration of about 70,000 ppm) leaving the desalination plant rather than fresh seawater.

Sodium chloride has traditionally been obtained from salt farms. The use of salt farm methods for the production of NaCl has been replaced in recent years in some countries by the ion-exchange membrane system. Japan, for example, produces 1,222,000 t/y by this method. This represents almost all of Japan's salt production [1]. Sand filters are used prior to feeding seawater to the dialyzers. A typical working area of the membranes is 340,000 m² and the average working time is 8080 h/y. The brine produced in this way has an average NaCl content of 163–182 g/l and a 90–95% purity of salt [(Na⁺ + K⁺)/Cl⁻]. The net power consumption of the dialysis is 306 kWh/t NaCl. Crystal salt is removed from the brine and concentrated in multi-stage vacuum evaporators (usually triple or quadruple effects). Most of these are of the forced-circulation type with outside heating. The heating area per evaporator is 700–1100 m².

In the Arabian Gulf two projects have already been established (in Kuwait and Abu Dhabi) which utilize desalination plant brines [2]. In the Abu Dhabi project, brine from the desalination plants is further concentrated and then

NaCl is crystallized in vacuum flash evaporators. The NaCl crystals are redissolved in pure water and then sent to caustic/chlorine cells for the production of sodium hydroxide and chlorine. Hydrogen and chlorine are used to form hydrochloric acid which may be used in the desalination plants for scale removal.

One of the attractive features of such schemes is that some of the products from the mineral extraction, such as NaOH, Cl_2 and HCl may be utilized in the nearby desalination plants.

However, if other minerals such as magnesium are also to be extracted from the desalination brines, complications will arise due to the fact that the pretreatment methods for fresh seawater fed to desalination plants may be incompatible with the downstream efficient recovery of these minerals. In such cases the potable water may be considered a by-product and the overall process designed primarily for the recovery of minerals such as MgCl_2 to produce magnesium metal [1].

When brines from solar concentration plants are used, brine pretreatment is necessary to remove bicarbonate (CO_3^{2-}) ions. This is necessary to prevent $\text{Mg}(\text{OH})_2$ scale formation on heat transfer surfaces in NaCl producing evaporators. However, when desalination brines are used as feedstock to the NaCl section, this pretreatment may not be necessary because the above pretreatment may already have been carried out in the desalination plant. It is worth noting that recent trends indicate that encouraging results were obtained when drained brines produced from multi-stage desalination plants are further concentrated by electrodialysis. The resulting high concentration salt solution is then fed to the caustic soda electrolysis plant. It has been reported [1] that the electrodialysis of such drained brines had produced concentrated brines containing 250 g/l NaCl. The electrodialysis current density employed was 6–7 A/dm^2 at a power consumption of about 300 kWh/t NaCl. Moreover, the total quantity of Ca^{2+} and Mg^{2+} ions in the concentrated brine can be reduced to 0.03 in terms of the equivalent ratio to Cl^- ions.

However, the electrodialysis approach was not considered in the economic evaluation in the present study because these processes are still at the research and development stage and reliable data relating to commercial scale-fixed and operating cost are missing.

Manufacturing steps

High-grade granulated salt can be crystallized out of desalination brines by multiple-effect vacuum evaporators (MEE), see Fig. 2. Such units operate essentially at low pressure with the pressure decreasing downwards the evaporator stages line. Steam can be passed either in co-current or counter-current flow schemes. In forward feed, all the brine enters the first or highest temperature stage where some concentration and crystallization takes place. The type

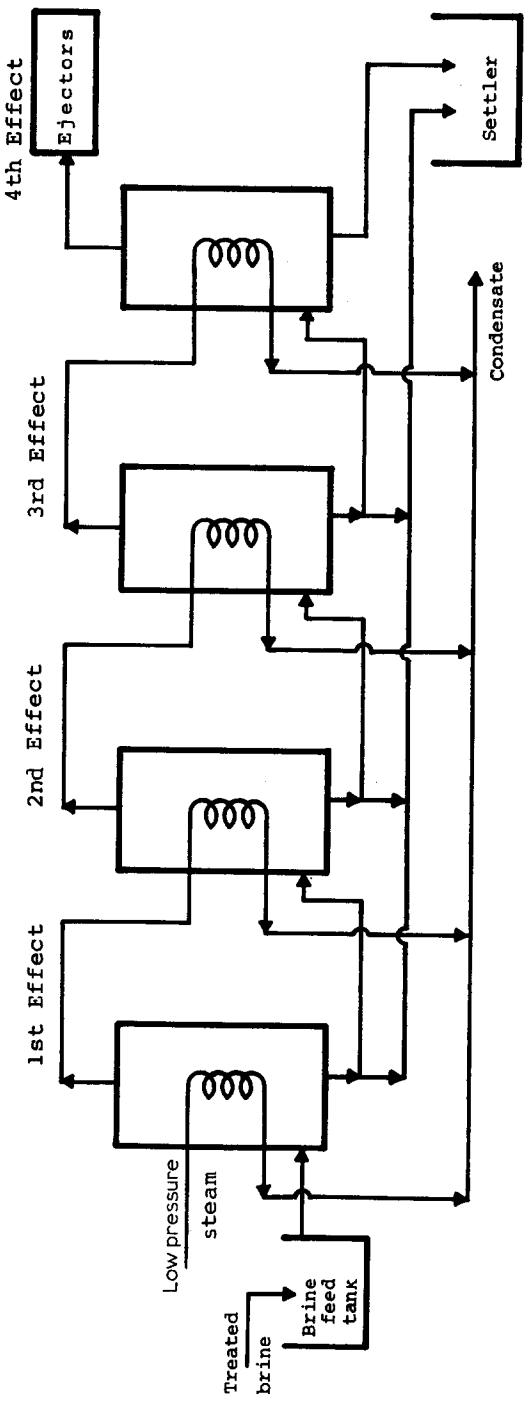


Fig. 2. Multiple-effect vacuum evaporators.

of feed arrangement used depends largely on the composition of the feed brine. However, forward feed is usually preferred because this arrangement involves a reduction in temperature as the solution is concentrated. Operation at lower temperatures minimizes corrosion and reduces calcium sulfate anhydride deposition [1].

The caustic/chlorine section of the plant can employ either a diaphragm or mercury cell. In either case salt produced in the MEE is transported initially from storage to the salt dissolvers (see Fig. 3).

In the salt dissolvers, NaCl is dissolved in fresh process water and process water recovered from caustic and salt evaporator/separator. Impurities harmful to the cells (such as magnesium and calcium) are removed by pretreatment.

Low voltage direct current is employed in the electrolysis. The weak soda-brine mixture leaving the electrolytic cell (containing about 11% caustic soda) is concentrated to about 50% in an MEE unit. Mercury cells have a relatively complex design compared to diaphragm cells but generally produce chlorine at lower cost.

Environmental considerations have induced manufacturers to switch from the mercury system (which causes mercury pollution) to the diaphragm system. It has been suggested that the feed to such cells might comprise of condensed brine obtained from electrodialysis of drained brine.

In the hydrochloric acid section, hydrochloric acid can be produced by combustion of hydrogen and chlorine. The purity of the ensuing acid depends upon the purity of the hydrogen and chlorine. As both of these gases are available in a very pure state from the electrolysis section of the plant, this synthetic method produces the purest hydrogen chloride of all the competing processes.

The reaction between H_2 and Cl_2 is highly exothermic and goes spontaneously to completion as soon as it is initiated. By carefully controlling the operating conditions, a manufacturer can obtain a gas containing 99% HCl. The HCl is further purified by absorbing it in water in a tantalum or impregnated graphite absorber. The aqueous solution is stripped of HCl under slight pressure, giving strong gaseous HCl which is dehydrated to 99.5% HCl by cooling to $-12^\circ C$. The section relating to HCl production is not included in the economic evaluation of this study.

Preliminary process economics evaluation assumptions:

- (1) It is assumed that the mineral extraction plant will be erected adjacent to the Al-Jubail desalination plant.
- (2) The desalination plant operates at a capacity of 253.5 mgd. The net brine discharge from this plant is about 371 mgd at 70,000 ppm TDS.
- (3) The mineral extraction plant utilizes only about 3% of the net brine discharge from the desalination plant.
- (4) The diaphragm cell produces 1.12 tons of caustic soda and 0.82 Gcal equiv-

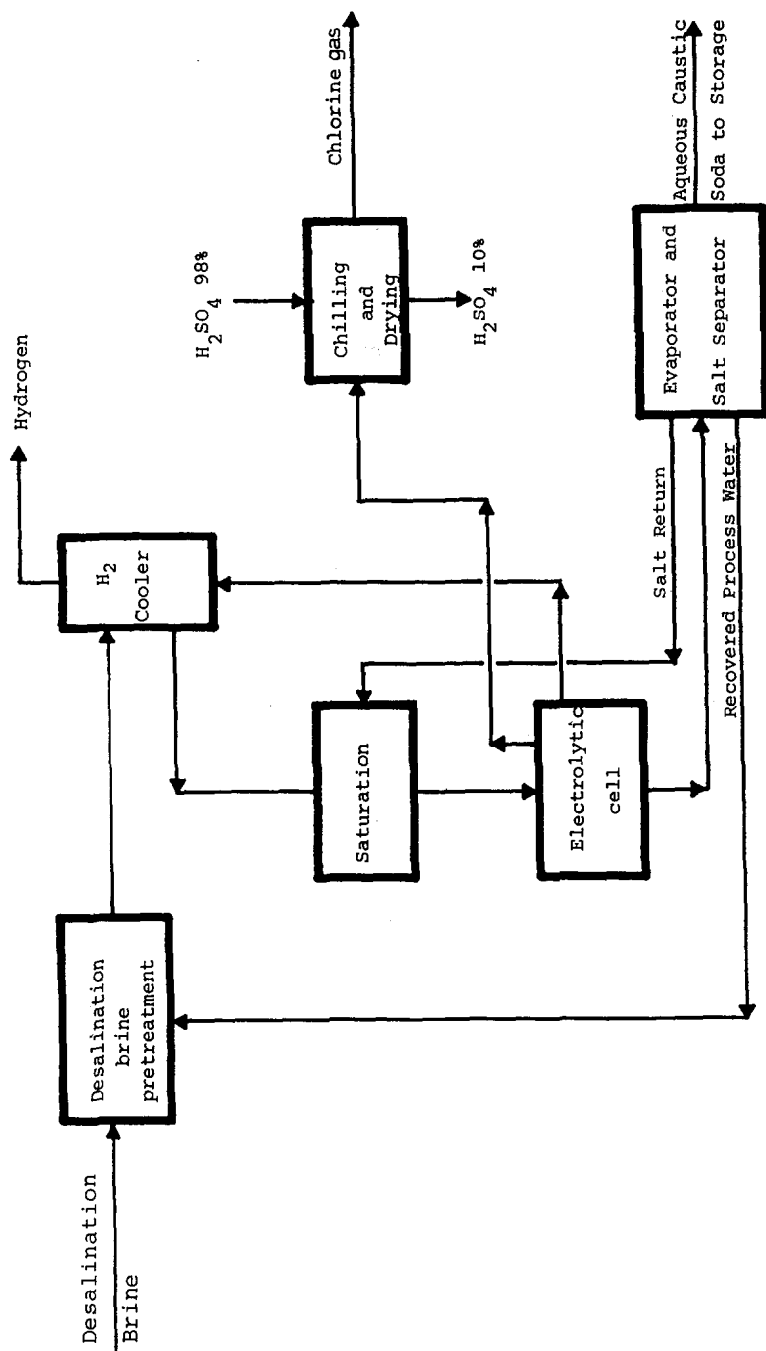


Fig. 3. Caustic/chlorine plant.

alent of hydrogen per ton of chlorine. On this basis the production capacity of the plant will be:

500,000 t*/y NaOH

446,430 t/y Cl₂

366,000 Gcal equivalent of H₂

Full marketability of the product mix is assumed.

(5) The brine is supplied free of charge to the mineral extraction plant.

(6) The utility costs are as follows:

Cooling water (seawater)	1.90 ¢/m ³
Steam	4.60 \$/Mt
Process water	80.00 ¢/m ³
Electricity (from local grid)	1.50 ¢/kWh
Natural gas	47.00 ¢/GJ
Fuel oil	42.38 \$/t

(7) Diaphragm rather than mercury cells will be used in the caustic/chlorine section of the complex.

Production cost basis:

Operating labour** (\$/h actually worked including costs of fringe benefits and shift overlap)	36.4
Operating supplies (% of operating labour)	10
Control laboratory (% of operating labour)	20
Plant overhead (% of operating labour plus maintenance labour plus control laboratory labour)	100
Taxes and insurance (%/y of total fixed investment)	2
Depreciation (% TFI)	10

Scope of cost estimates

The plant location is the industrial area in Al-Jubail, Kingdom of Saudi Arabia, 1987. For this reason the cost estimates exclude the cost of dock facilities (seawater for cooling purposes). Start-up, commissioning and infrastructure facility cost are also excluded.

Total capital investment

The plant-fixed investment cost (Al-Jubail, 1987) is estimated as follows ($\times 10^3$ \$):

Desalination brine concentration section	584
Freeze crystallization for sodium sulfate extraction section	31,969

*t = metric ton = 1000 kg.

**Assuming 1750 h per job per year.

Freeze crystallization of brine from previous section to produce NaCl in 23.3% solution	17,655
Caustic/chlorine section* (using diaphragm cells)	<u>459,705</u>
Total fixed investment	509,913

Total product cost (\$/t NaOH produced):

Feedstocks (transportation cost)	10.00
Anode requirements + chemicals	15.00
Electricity (3.416 MWh/t)	66.24
Cooling water (325 t/t)	6.18
Fuel	4.08
Low-pressure steam (3.13 t/t)	14.40
Process water (4.3 t/t)	3.44
Operating supplies	2.01
Control laboratory	4.02
Plant overhead	6.03
Taxes and insurance	5.89
Depreciation	101.98
By-product credits:	
Cl ₂	-89.00
H ₂	<u>-1.45</u>
Total product cost	148.82

For comparison purposes are here the Western Europe caustic soda prices in October 1987:

Liquid (Market), DM 400–470 per DMT FD
 Diaphragm (Spot), \$250–280 per DMT FOB NWE/Med
 Mercury (Spot), \$260–285 per DMT FOB NWE/Med
 Fused (Spot), \$320–340 per ton FOB NWE
 Flakes (Spot), \$330–360 per ton FOB NWE/Med
 Pearls (Spot), \$330–360 per ton FOB NWE

CONCLUSIONS

The availability of very large quantities of highly concentrated brines from desalination plants in the Kingdom of Saudi Arabia provides a strong incentive for exploring the techno-economic feasibility of extracting some valuable minerals from these brines. The preliminary economic evaluation in this study

Based on a 1982 cost (Western Europe) of $\$177 \times 10^6$ for a production capacity of 183,000 t/y of caustic soda. A location factor of 1.3 has also been assumed.

indicates that caustic soda can be produced at Al-Jubail industrial area at a cost of about 149 \$/t. The proposed plant has benefited greatly by the free availability of the feedstock brine and by the low cost of electricity and fuel. The most important cost items were depreciation, power and the by-product credit of co-produced chlorine. The production cost of caustic soda is highly sensitive to any variation in any of these cost items. The estimated production costs favourable in view of the caustic soda prices in Western Europe in October, 1987.

REFERENCES

- 1 Sea water desalination technology, Japan International Cooperation Agency, March 1979.
- 2 Mineral recovery from sea water, Unpublished report by DSS engineers to GOIC, 1987.
- 3 Desalting Plants Inventory Report No. 8, International Desalination Association, Topsfield, MA, February 1985.